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Respectfully submitted,

[Page 1 of 2]

Date March 25, 2005

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Docket Number: 11321-P086V1

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Docket Number 11321-P086V1

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Number 1 of 1

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FUNCTIONALIZATION OF CARBON NANOTUBES IN SUPER ACID MEDIUM

This work was supported by the National Science Foundation, Grant Number DMR-0073046; University of Washington (pass through from AFSOR, Grant Number F49620-01-1-0364); TAMU/TEES, Grant Number NASA NCC-01-0203; National Aeronautics and Space Administration, Grant number JSC-NCC-9-77; and Office of Naval Research, Grant Number N00014-02-1-0752.

Description of the Invention

General Purpose. The present invention is directed to processes that exploit the solubility of carbon nanotubes in super acid media (*e.g.*, oleum = fuming sulfuric acid = H_2SO_4 plus SO_3) to covalently attach functional groups to the sidewalls of carbon nanotubes. This affords individual functionalized carbon nanotubes that are dispersible in a variety of matrices. Such solubility of carbon nanotubes in super acid media is described in PCT Patent Application Publication No. WO 01/30694 A1 by Smalley *et al.* and United States Patent Application Publication No. US 2003/0170166 A1 by Smalley *et al.* Such materials are likely to provide optimal properties in many potential materials applications.

Technical Description. While the making and/or using of various embodiments of the present invention are discussed below, it should be appreciated that the present invention provides many applicable inventive concepts that may be embodied in a variety of specific contexts. The specific embodiments discussed herein are merely illustrative of specific ways to make and/or use the invention and do not delimit the scope of the invention.

Purified single wall carbon nanotubes (0.050 g, 4.2 mmol), (prepared according to Chiang, I. W.; Brinson, B. E.; Huang, A. Y.; Willis, P. A.; Bronikowski, M. J.; Margrave, J. L.; Smalley, R. E.; Hauge, R. H. *J. Phys. Chem. B* 2001, 105, 8297) were dispersed in oleum (50 mL, 20% free SO_3) at 80 °C. This dispersion was then filtered over glass wool to remove any large particulate. Sulfanilic acid (2.91 g, 16.8 mmol) was added to the dispersion followed by

sodium nitrite (1.16 g, 16.8 mmol). Finally 2,2'-azo-*bis*-isobutyronitrile (1.38 g, 8.4 mmol) was added to provide a radical source. This solution was allowed to stir at 80 °C for one hour at which point the reaction mixture was poured into 300 mL of water. This mixture was then filtered over a polycarbonate membrane filter (1 µm pore size), and washed with 500 mL of acetone. The resultant black powder, **1**, was then dispersed in water and filtered to be certain any soluble impurities are removed. At this point the material is ready for use or characterization.

Note the attached file of the Raman spectrum (Fig. 1) and the UV/Vis spectrum (Fig. 2) of **1** where the transitions are clear that functionalization has occurred. Most importantly, however, notice the atomic force microscopy (AFM) image (Fig. 3) and corresponding section analysis (Fig. 4) of **1** where many single tubes are formed and they do not tend to re-rope. This material was not centrifuged prior to imaging, and there is no surfactant present. For a description of the spectral characterization utilization, see: Bahr, J. L.; Tour, J. M. "Covalent Chemistry of Single-Wall Carbon Nanotubes—A Review," *J. Mater. Chem.* 2002, 12, 1952-1958. And for non-bundling tubes, generated by surfactant wrapping followed by functionalization, see: Dyke, C. A.; Tour, J. M. "Unbundled and Highly Functionalized Carbon Nanotubes from Aqueous Reactions," *Nano Lett.* 2003, 3, 1215-1218; and Dyke, C. A.; Tour, J. M. "Overcoming the Insolubility of Carbon Nanotubes through High Degrees of Sidewall Functionalizing," *Chem. Eur. J.* 2004, 10, 812-817.

Interestingly, and significantly, when sulfanilic acid was used as described, stable water suspensions of the functionalized nanotubes could be generated. The suspensions did not settle even after one week.

Utility. The most immediate and obvious use of this procedure is the production of individual carbon nanotubes by a process that is highly scaleable. It is widely accepted that individual carbon nanotubes are necessary to achieve optimum properties in many potential applications. To date, no process exists to reliably produce individual carbon nanotubes on a bulk scale. The present invention eliminates the need for using fluorine, sonication, and centrifugation which previous methods for generating individual carbon nanotubes have relied upon (a). Fluorine use, sonication and centrifugation are frowned upon heavily by industry due to the difficulty in scaling these processes. Furthermore, the present invention eliminates the use of surfactant-

wrapping of carbon nanotubes followed by sonication and centrifugation (b). Both methods (a) and (b) could never be scaled to provide a process that affords individualized nanotubes in the quantities needed for materials applications in bulk. The protocol disclosed here eliminates the need for centrifugation and wrapping, and it capitalizes on the use of Rice-patented protocols on diazonium functionalization by simply providing a solvent change for the reaction medium. See PCT Patent Application Publication No. WO 02/060812 A2 by Tour *et al.*; PCT Patent Application No. US03/22072 by Tour *et al.*; Bahr *et al.*, "Functionalization of Carbon Nanotubes by Electrochemical Reduction of Aryl Diazonium Salts: A Bucky Paper Electrode," *J. Am. Chem. Soc.*, 123:6536-6542 (2001); and Dyke *et al.*, "Solvent-Free Functionalization of Carbon Nanotubes," *J. Am. Chem. Soc.*, 125:1156-1157 (2003).

Novelty. Presently, no other method exists to functionalize single wall carbon nanotubes using a super acid solvent.

Steps Involved. In some embodiments, the invention is a process involving the following steps:

1. Oxidatively treated single wall carbon nanotubes are dispersed with stirring in oleum to form a dispersion/solution.
2. The dispersion/solution is filtered over glass wool to remove any impurities.
3. An aniline of choice is added to form a reaction mixture.
4. Sodium nitrite followed by a radical source is then added cautiously to the reaction mixture.
5. The mixture is heated and stirred for one hour.
6. The mixture is diluted with water, filtered, and washed with acetone.
7. The resultant solid (functionalized single wall carbon nanotubes) is suspended in water and filtered again to remove impurities.

Variations. Such processes are applicable to other carbon nanotubes such as multi-wall carbon nanotubes. The super acid used in this example is oleum but the process is by no means limited to this medium. Chlorosulfonic and triflic acid are examples of other readily available super acids which would be viable alternatives to oleum. Sulfanilic acid is the aniline used in the above example but any aniline is a possible variation. Under the conditions here, using sulfanilic acid or other anilines that might sulfonate, water soluble nanotubes are yielded. In this particular example 2,2'-azo-bis-isobutyrylnitrile was used as a radical source. Any substance that is known to break down into radicals at relatively low temperatures may be used as a substitute such as benzoyl peroxide and di-tert-butylperoxide. The addition of radical source may not be essential, but it is desirable. It may be that only small amounts of super acid are needed, such as super acid sufficient to merely make a paste of the mixture, following the protocol of our previously disclosed solvent-free (solvent-wetted) disclosures. See PCT Patent Application No. US03/22072 by Tour *et al.* One could use the pre-formed diazonium salt as well as the aniline/nitrite (alkyl nitrite or sodium nitrite) combinations disclosed here.

There are several other variations that are notable that make this procedure more general.

- (A) Concentration. The concentration of the reaction can vary widely from fractions of a milligram of nanotubes per mL of super acid to paste-like conditions wherein the mechanical action of a stirring system on the super acid-wetted tubes results in exfoliation and reaction of individual nanotubes with the reactant. For a complete description of solvent-wetted reactions or paste-like conditions, see: Dyke, C. A.; Tour, J. M. "Solvent-Free Functionalization of Carbon Nanotubes," *J. Am. Chem. Soc.*, 2003, 125, 1156-1157.
- (B) In addition to the diazonium reactions described previously, this process should be general to a host of organic and organometallic reactions provided that the reagents are sufficiently reactive in the super acid medium for a sufficiently long time for the reaction to take place. Below is a partial list of the reactions that could be possible. For example, use of:
 - a. Cationic intermediates should cause reaction with the nanotubes. For example, use of isopropanol should cause the isopropyl cation to form that would react with the pi-electron rich nanotubes since the nanotubes are the only nucleophilic

species in solution. Likewise, cations can be generated from any alkene or alkyne. Generally, these could be termed Friedel-Crafts-type reactions where the nanotube acts as the nucleophile toward an electrophilic species. The electrophiles could be:

- i. carbocations such as alkyl, alkenyl, alkynyl, aryl, aceyl (RCO^+) cations
 - ii. halonium ions such as Cl^+ , Br^+ , I^+ or F^+ species
 - iii. metal cations, specifically transition metals and group III-A through VI-A metals.
 - iv. Other known types of species used in Friedel-Crafts reactions
- b. Dipolorophiles should be amenable to this reactions such as the Prato dipolorophile reaction (Georgakilas, V.; Kordatos, K; Prato, M.; Guldi, D. M.; Holzinger, M.; Hirsch, A. *J. Am. Chem. Soc.* 2002, *124*, 760.) or nitrile oxide reaction (Meier, M. S.; Poplawska, M. *J. Org. Chem.* 1993, *58*, 4524.) or trimethylene methane-derivatives. Also, ylides should be useable in this process.
- c. Benzyne addition (from anthranilic acid and isoamyl nitrite) (Meier, M. S.; Wang, G.-W.; Haddon, R. C.; Brock, C. P.; Lloyd, M. A.; Selegue, J. P. *J. Am. Chem. Soc.* 1998, *120*, 2337) or 2-(trimethylsilyl)phenyltrifluoro-methanesulfonate treated with TBAF, which has been shown to give benzyne (Himeshima, Y.; Sonoda, T.; Kobayashi, H. *Chem. Lett.* 1983, 1211).
- d. Radical reactions, in general. Radical intermediates can be generated thermally, photochemically or chemically using initiators or sensitizers and this chemistry is compatible with super acid. So any radical source should have a possibility of adding to the nanotubes. This includes:
- i. Carbon radicals such as alkyl, alkenyl, alkynyl, aryl, aceyl (RCO^\cdot) radicals
 - ii. halogen radical species
 - iii. heter-atom radical species such as oxy radicals
 - iv. metal-based radicals, specifically transition metals and group III-A through VI-A metals.

- e. Oxidation reactions such as reaction with
 - i. peroxyacids
 - ii. metal oxidants such as osmium tetroxide, potassium permanganate, chromates
 - iii. ozone
 - iv. oxone
 - v. oxygen
 - vi. superoxides
 - f. Reductants such electrochemical reductants or other species that are super acid-compatible.
 - g. Heteroatomic nucleophiles where the nucleophile bears a lone pair of electrons such as sulfides or thiols.
 - h. Carbenes.
 - i. Dienes that could react with the tubes such that the tubes act as a dieneophile in a Diels-Alder Reaction.
- (C) The process disclosed here used heat, but room temperature processes are also effective on other anilines.
- (D) Other anilines used successfully to date are aniline (aminobenzene) which sulfonates under the same reaction conditions, 2-(4'-aminophenyl)ethanol, 4-chloroaniline, 4-iodoaniline, 4-tert-butylaniline, and 4-nitroaniline. This shows the generality of the process.
- (E) Although the nanotubes used here were oxidatively treated to purify the sample, this protocol can also be used on the crude, as provided nanotubes.

All patents and publications referenced herein are hereby incorporated by reference. It will be understood that certain of the above-described structures, functions, and operations of the above-described embodiments are not necessary to practice the present invention and are included in the description simply for completeness of an exemplary embodiment or

embodiments. In addition, it will be understood that specific structures, functions, and operations set forth in the above-described referenced patents and publications can be practiced in conjunction with the present invention, but they are not essential to its practice. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without actually departing from the spirit and scope of the present invention as defined by the appended claims.

WHAT IS CLAIMED IS:

1. A method comprising the steps of:
 - a) dispersing single-wall carbon nanotubes in a super acid medium to form a dispersion;
 - b) adding aniline species and sodium nitrite to the dispersion to form a reaction mixture; and
 - c) reacting the reaction mixture to form functionalized single-wall carbon nanotubes.
2. The method of Claim 1, wherein the single-wall carbon nanotubes have been oxidatively treated.
3. The method of Claim 1 or 2, wherein the single-wall carbon nanotubes are homogeneous in a characteristic selected from the group consisting of length, diameter, chirality, and combinations thereof.
4. The method of Claims 1-2, or 3 further comprising a step of filtering the dispersion to remove any large particles.
5. The method of Claims 1-3, or 4, wherein the super acid medium is selected from the group consisting of oleum, chlorosulfonic acid, triflic acid, and combinations thereof.
6. The method of Claims 1-4, or 5, wherein the aniline species comprises sulfanilic acid.
7. The method of Claims 1-5, or 6 further comprising a step of adding a radical source to the reaction mixture.
8. The method of Claim 7, wherein the radical source is selected from the group consisting of 2,2'-azo-bis-isobutyronitrile, benzoyl peroxide, di-tert-butylperoxide, and combinations thereof.
9. The method of Claims 1-7, or 8, wherein the step of reacting comprises heating and stirring.
10. The method of Claims 1-8, or 9 further comprising the steps of:
 - a) diluting the reaction mixture with water, subsequent to forming functionalized single-wall carbon nanotubes, to form a diluted reaction product mixture;

- b) filtering the diluted reaction product mixture over a filter to isolate the functionalized single-wall carbon nanotubes; and
 - c) washing the isolated functionalized single-wall carbon nanotubes with a washing solvent to obtain washed functionalized single-wall carbon nanotubes.
11. The method of Claim 10, wherein the washing solvent is acetone.
12. The method of Claim 10 or 11 further comprising the steps of:
- a) re-suspending the washed functionalized single-wall carbon nanotubes in water to form a re-suspension;
 - b) filtering the re-suspension to recover re-washed functionalized single-wall carbon nanotubes.

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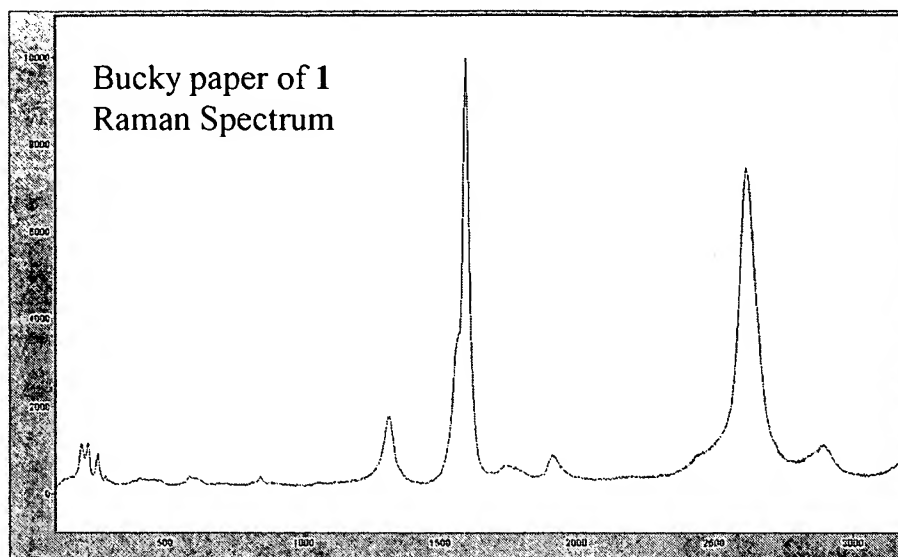
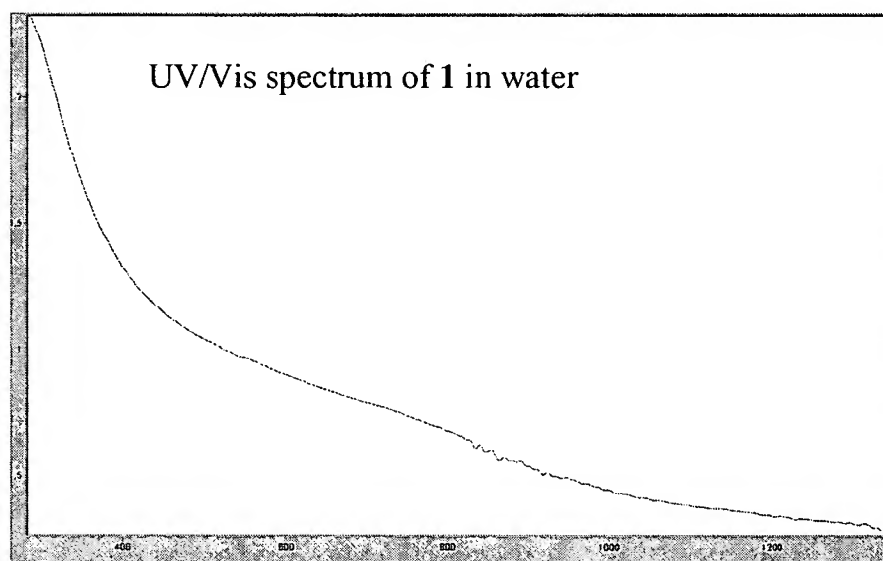
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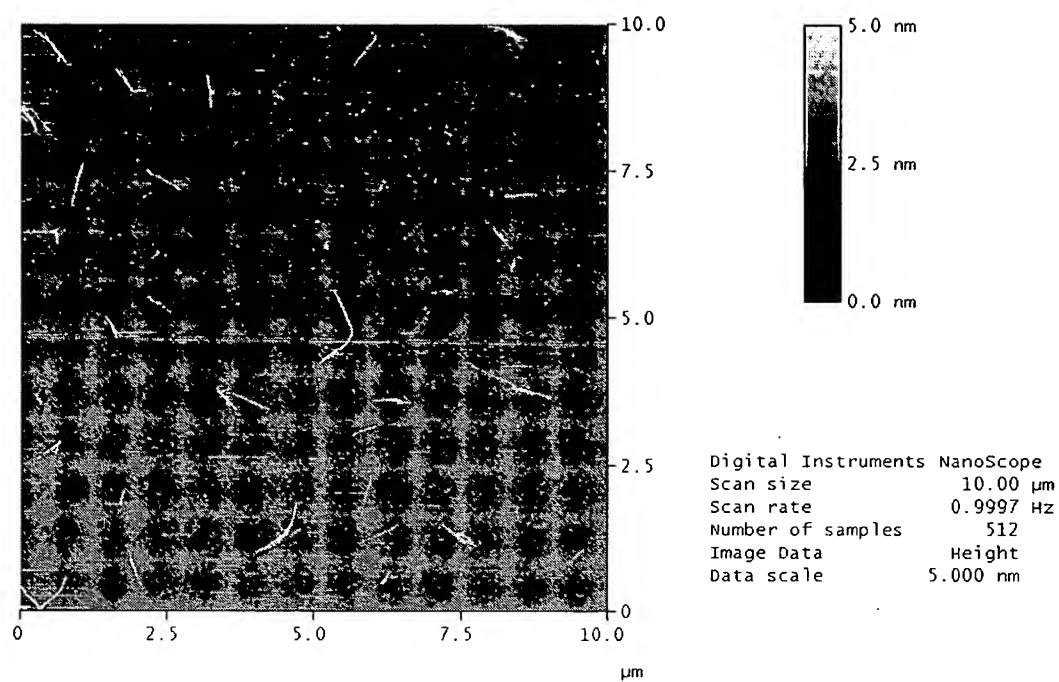
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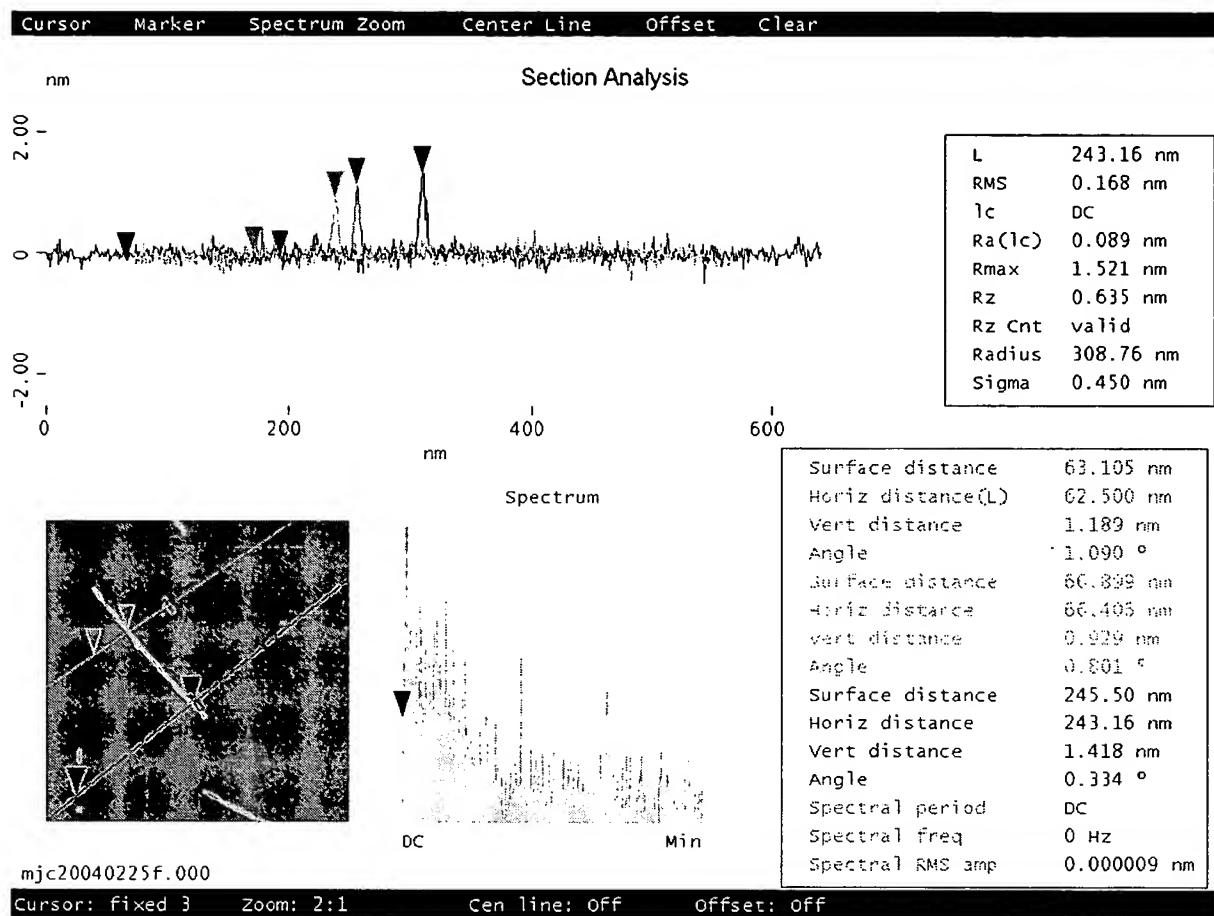
*Fig. 1**Fig. 2*



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AFM image of **1** showing many individual functionalized single-wall carbon nanotubes.

Fig. 3



AFM image of 1 showing an individual nanotube section analysis.

Fig. 4